

A Further Investigation of
Paradiazotoluene Sulphate and the Action
of Sulphuric Acid on the Methyl
Ether of Paracresol

A DISSERTATION

PRESENTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

—BY—

GELLERT ALLEMAN

1897

EASTON, PA.:
CHEMICAL PUBLISHING CO.
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This investigation was undertaken at the suggestion of Prof. Ira Remsen, and was carried on under his constant supervision.

I wish to express my most sincere thanks to Prof. Remsen for the interest he has manifested, the advice he has given, and the kindness he has shown me on all occasions. I would also express my obligations to Prof. Morse, Prof. Ames, and to Dr. Mathews.

A FURTHER INVESTIGATION OF PARADIAZO- TOLUENE SULPHATE AND THE ACTION OF SULPHURIC ACID ON THE METHYL ETHER OF PARACRESOL.

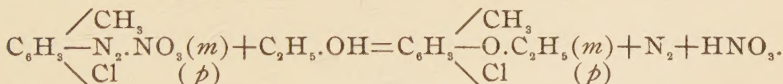
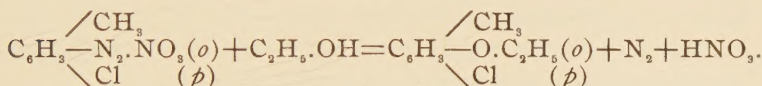
Introduction.

Griess, in his extensive investigation of diazo compounds, studied their decomposition under the influence of various reagents. He thought that when they were decomposed with boiling alcohol the diazo group was replaced by hydrogen. Thus he supposed that when diazo benzene nitrate was decomposed by alcohol the reaction took place as follows :



This is known as the Griess, or hydrogen reaction.

In decomposing the two isomeric diazoparachlortoluidines with alcohol, Wroblewsky, in 1870, found that the reactions involved might be represented by the following equations :



This is known as the ethoxy reaction ; the term for similar reactions with alcohols in general being known as the alkoxy reaction.

Numerous investigations since then have shown that, in many cases, the hydrogen and alkoxy reactions take place simultaneously when the diazo compound is decomposed with alcohols. In 1882, Prof. Remsen¹ suggested that the presence and position of other groups in the benzene nucleus might influence the action. Numerous investigations have been carried on in this laboratory under the direction of Prof. Remsen, by Orndorff,² Palmer,³ Graham,⁴ Dashiell,⁵ Metcalf,⁶

¹ Am. Chem. J., 4, 377.

² Ibid, 9, 387.

³ Ibid, 8, 243.

⁴ Ibid, 11, 319.

⁵ Ibid, 15, 124.

⁶ Ibid, 15, 301.

Parks,¹ Shober,² Beeson,³ Weida,⁴ Cameron,⁵ Chamberlin,⁶ and Bromwell.⁷ It was found that the reaction was markedly influenced by the character and position of the groups in the nucleus, by the pressure and temperature at which the decomposition was effected and by the kind of alcohol used.

Chamberlin⁸ found that by decomposing the nitrate or sulphate of paradiazotoluene with methyl alcohol, under ordinary, diminished, or increased pressure, both paramethoxytoluene and toluene resulted. He also confirmed the observation of Remsen and Dashiell⁹ that lowering the temperature and pressure favors the hydrogen reaction in the case of the diazo nitrate, and that the sulphate gives a better yield of the methoxy product as the pressure decreases. Chamberlin also studied the decomposition of the sulphate and nitrate of paradiazotoluene with methyl alcohol in the presence of potassium hydroxide, potassium carbonate, and zinc dust, and found that under these conditions only toluene was formed.

At the suggestion of Prof. Remsen, the writer undertook the present investigation to determine, if possible, what influence the presence of the nitro compounds (formed in the diazotizing process) would have, when the diazo compound was decomposed with methyl alcohol.

Preliminary Experiments for the Preparation of the Diazo Compound.

A number of experiments were made for the purpose of finding out what method would yield the largest amount of the compound sought.

I. The neutral paratoluidine sulphate was made according to Wellington,¹⁰ by treating one molecule of paratoluidine with one and one-half molecules of sulphuric acid. It was crystallized and then analyzed in order to be sure of its composition. The neutral sulphate thus prepared was dissolved in methyl alcohol, the flask containing the solution placed in ice-water and nitrous fumes, somewhat cooled by being first passed

¹ *Am. Chem. J.* **15**, 320. ² *Ibid.* **15**, 379. ³ *Ibid.* **16**, 244. ⁴ Dissertation, 1894.

⁵ Dissertation, 1894.

⁶ Dissertation, 1894.

⁷ Dissertation, 1895.

⁸ Dissertation, 1894.

⁹ *Loc. cit.*

¹⁰ *Ber. d. chem. Ges.*, **18**, 3311.

through gas bottles surrounded by cold water, were passed into the solution for several hours. A very small amount of red flaked crystals appeared, and these were taken out, washed with ether in order to remove the red coloring matter, a weighed portion dissolved in water and quickly titrated with a standard solution of ammonia. The result showed the crystals to be ordinary paradiazotoluene sulphate. It was thought that a neutral diazo sulphate might be formed and be contained in the solution, but efforts to isolate it, if it were formed, were unsuccessful.

As there still remained the possibility that the diazo compound might be held in solution, the flask was provided with a return-condenser, placed on a water-bath and the decomposition of the diazo compound remaining in the flask, with the methyl alcohol, effected. The excess of alcohol was then distilled off and the liquid remaining in the flask treated with three times its volume of water. A very small amount of the oil separated by distillation with steam. This oil, from its boiling-point, proved to be the methyl ether of paracresol, but the yield being so poor, the method described was abandoned.

II. Acid paratoluidine sulphate was prepared, as directed by Wellington,¹ by treating one molecule of paratoluidine with three and one-half molecules of sulphuric acid. It was dissolved in methyl alcohol and diazotized as described for the neutral compound. The yield of paradiazotoluene sulphate was fairly good, but far from quantitative—ninety grams of paratoluidine sulphate yielding thirty-nine grams of paradiazotoluene sulphate.

III. The chloride of paratoluidine was then made. This was placed in methyl alcohol and nitrous fumes passed into it until the diazotization was complete. This took a somewhat longer time than that in which the acid sulphate was diazotized. The yield of the diazo compound was about the same as that obtained from the acid sulphate.

The method finally adopted which gave the best results, in-

¹ *Loc. cit.*

volves a very slight change from that under II above described, and is as follows:

Preparation of the Paradiazotoluene Sulphate.

One hundred grams of paratoluidine were placed in an Erlenmeyer flask of one liter capacity, and 500 grams of anhydrous methyl alcohol added. As soon as complete solution took place, 100 grams concentrated sulphuric acid were added by means of a dropping funnel, allowing only a few drops into the flask at one time. Even with the slow addition of the acid and constant shaking of the flask, it was found necessary to place the flask in cold water to prevent loss of the alcohol on account of the heat generated by the reaction. As soon as a slight excess of sulphuric acid is added, the precipitate of paratoluidine sulphate which first separates goes into solution and does not again appear when the flask is placed in water containing ice.

The flask is then surrounded by ice-water, and a rapid current of nitrous fumes passed through the solution for about thirty minutes. The fumes were cooled before being conducted into the vessel by first being passed through two gas bottles which were placed in cold water. After a time, crystals of paradiazotoluene sulphate appear in the flask. They have a red color, but on being washed with ether the color disappears, showing the crystals to be glistening, snow-white flakes. The fumes are conducted through the solution till a few drops of the removed liquid, on treatment with dilute caustic soda, no longer give the odor of paratoluidine.

The diazo compound when dry is a comparatively stable body. Crystals were kept in a desiccator for six weeks without the least evidence of decomposition. If the crystals be filtered off and the filtrate be allowed to stand in a cool place, perfectly transparent, almost colorless prisms will crystallize from the solution.

Decomposition of the Diazo Compound with Methyl Alcohol.

Instead of taking the crystals of paradiazotoluene sulphate out of the flask and purifying them by washing with ether

and then effecting the decomposition, as is usually done in analogous cases, the flask was provided with a return-condenser, and placed on a water-bath. Decomposition began at the ordinary temperature, but it was slight. At about 60° the decomposition was rapid and the reaction had to be checked at times, in order to keep the liquid from frothing up the inner tube of the condenser. This was done by pouring cold water on the outside of the flask. After the evolution of gas had almost ceased, the temperature was raised and the liquid boiled rapidly for twenty minutes, in order to make sure that the decomposition was complete.

It will be seen from the above statements that the decomposition was effected in the presence of all those compounds which were formed in the flask during the diazotizing process.

Separation and Purification of the Methyl Ether of Paracresol.

After it was judged that the decomposition had been completely effected, several portions were placed in a large balloon flask provided with a Hempel tube about three feet high. The methyl alcohol was then distilled and some toluene came over with it, showing that the hydrogen reaction had also taken place. When the distillation was conducted too fast it was found that some of the oil came over with the alcohol. As soon as the thermometer at the top of the Hempel tube rose above 64° , the distillation was discontinued and, after the solution had cooled somewhat, water was added to the flask. The distillation was then continued and quite a quantity of methyl alcohol passed over, showing that methylsulphuric acid was, in all probability, formed and that it broke down on the addition of water. After the methyl alcohol was removed as completely as possible by this method, the contents still remaining were treated with about two times the volume of water. The flask was then connected with a condenser, placed on a sand-bath and heated almost to the boiling-point of the liquid contained in it. On passing steam through the mixture, a yellow oil came over with the distillate. This oil has an extremely great surface tension. When nearly all

the oil had passed over, it was noticed that the last portions were of a red color. The oil was then separated by means of a separating-funnel, dried with calcium chloride, placed in a distilling-bulb and, after several distillations, a product was obtained which boiled at 174° – 176° . This is the methyl ether of paracresol described by Körner,¹ and also obtained by Chamberlin,² who gives its boiling-point as $174^{\circ}.5$ (corr.) Its identity was established by oxidation with potassium permanganate, anisic acid being formed.

It was thought that probably the oil which came over above 180° might have its boiling-point raised by the presence of nitro compounds and for the purpose of removing the latter, in case they were present, the whole portion of the high-boiling oil was treated with granulated tin and hydrochloric acid. After treatment in this manner, it was washed repeatedly with water and finally dried with calcium chloride. It was then distilled, and nearly the entire portion passed over between 174° and 176° , showing that the rise in the boiling-point of a portion of the oil was undoubtedly due to the influence of nitro compounds which can be removed by the well-known method above described.

The tar which remained in the flask into which steam had been passed, was dissolved in alcohol and the alcohol slowly evaporated, but no crystals were obtained. It was then treated with ligroïn, from which yellow needles separated. These needles melted at 74° – 79° . Chamberlin investigated this tarry material, and found that it contained dinitroparacresol, $(\text{CH}_3.\text{NO}_2.\text{OH}.\text{NO}_2.1 : 3 : 4 : 5)$. He found the melting-point of this substance to be $80^{\circ}.5$ (corr.), and accounts for its formation by the fact that nitric acid is formed in the flask and acts on the paramethoxytoluene. He obtained the dinitroparacresol by the treatment of the methyl ether of paracresol with strong nitric acid and glacial acetic acid.

Action of Sulphuric Acid on Paramethoxytoluene.

The paramethoxytoluene was poured into pure concentrated sulphuric acid contained in an Erlenmeyer flask. The pro-

¹ Zeit. für chemie, 1868, p. 326.

² Dissertation, 1894.

portions in which the two compounds were brought together were three grams of sulphuric acid to one gram of paramethoxytoluene. The mixture assumed a dark red color and became warm, indicating that some action took place at the ordinary temperature. The flask was placed on a water-bath and heated till a few drops of its contents dissolved in water without cloudiness, showing that the paramethoxytoluene had been completely transformed into a sulphonic acid. On cooling, part of the sulphonic acid separated as yellow crystals.

The sulphonic acid thus obtained was then dissolved in water, poured into a large porcelain evaporating dish, and the solution gently heated. Finely powdered barium carbonate was slowly added until it was present in excess. After all the carbon dioxide had been expelled, the solution was filtered through muslin and the barium sulphate and the excess of barium carbonate repeatedly washed with hot water in order to remove any soluble barium salt which might be held mechanically by the insoluble salts. On concentrating the filtrate, the barium salt crystallized. It is a pure white semi-crystalline material, very soluble in cold water, and insoluble in alcohol. Attempts to obtain definite crystals by repeatedly crystallizing the salt under different conditions of concentration gave negative results.

Preparation of Paramethoxymetatoluenesulphonic Acid.

This acid was separated by adding to the aqueous solution of the barium salt above described sufficient dilute sulphuric acid to exactly precipitate the barium. After the barium sulphate had settled to the bottom, it was filtered off, washed with hot water and the filtrate evaporated on a water-bath to a small volume. On allowing the solution to cool, the free acid separates as yellow, flaked crystals. The acid is extremely soluble in water—one part dissolving in about half its weight of water. It is almost insoluble in ether, benzene, and ligroïn, but dissolves readily in methyl and ethyl alcohol and hot acetone.

It was thought that the acid was not perfectly pure on ac-

count of the fact that the sodium and copper salts made from it were colored differently from the same salts made from the barium salt. Attempts to obtain the acid in a colorless condition by treatment with animal charcoal, boiling it with ether and crystallizing it repeatedly from methyl and ethyl alcohol and from acetone, were unsuccessful. It was subsequently found that the color could be removed by washing the acid with cold anhydrous ether. If, after treatment in this manner, it is crystallized from alcohol, perfectly colorless, long prisms can be obtained, which melt at 105° – 108° . The prisms have a hexagonal appearance.

The evidence that this is a monosulphonic acid, and that the SO_2OH group entered in the meta position will be presented later.

Salts of Paramethoxymetatoluenesulphonic Acid.

All the salts which were made from this acid are extremely soluble in water.

In order to prepare them for analysis, the crystals were removed from the solution and rapidly dried by pressing them between layers of drying paper.

Sodium Salt, $\text{C}_6\text{H}_3 \begin{array}{c} \diagup \text{CH}_3 \\ \text{—SO}_2\text{ONa} \\ \diagdown \text{OCH}_3 \end{array} + \frac{1}{2}\text{H}_2\text{O}$.—This salt was made

by exactly neutralizing an aqueous solution of the free sulphonic acid by means of sodium carbonate. The salt at first crystallized in small orange-colored needles. Upon recrystallizing, colorless prisms were obtained. If allowed to stand in the air any length of time they effloresce.

Another sodium salt was prepared by exactly precipitating the barium, in an aqueous solution of the barium salt, by means of a dilute solution of sodium sulphate. After filtering off the barium sulphate, and evaporating the solution to a small volume, perfectly transparent, colorless needles separated. These, on exposure to the air, also lost water and turned white.

Analyses show that both of the salts prepared as described

above are identical in their composition. They are insoluble in strong, boiling alcohol. Analysis for sodium and water gave the following results :

	Calculated for $\text{C}_6\text{H}_3\left(\begin{smallmatrix} \diagup \text{CH}_3 \\ \text{—SO}_3\text{Na}+\frac{1}{2}\text{H}_2\text{O} \\ \diagdown \text{OCH}_3 \end{smallmatrix}\right)$	Found.		Salt from Ba salt.	
		I.	II.	III.	IV.
H_2O	3.86	3.96	3.98	3.89	3.92
Na	9.87	9.88	9.72	10.04	10.07

Potassium Salt, $\text{C}_6\text{H}_3\left(\begin{smallmatrix} \diagup \text{CH}_3 \\ \text{—SO}_2\text{OK} \\ \diagdown \text{OCH}_3 \end{smallmatrix}\right) + 2\text{H}_2\text{O}$.—A hot solution of

the free sulphonic acid was carefully neutralized with pure potassium carbonate. Transparent, slightly colored red needles were first obtained and, on recrystallizing these, good-sized prisms, which had a slight yellow color, separated. The analysis of these prisms showed that a slight amount of potassium carbonate had come down with the crystals. The salt was purified by boiling it with 50 per cent. alcohol from which it crystallizes, when the solution is concentrated, in colorless needles which radiate from the central point; from dilute solutions, in thin flakes. The salt is much less soluble in water than any of the other salts of this acid. It is insoluble in boiling strong alcohol.

0.1547 gram of salt lost, at 200° , 0.0206 gram H_2O , and gave 0.0483 gram K_2SO_4 or 0.02165 gram K.

0.2582 gram of salt lost, at 200° , 0.0339 gram H_2O , and gave 0.0812 gram K_2SO_4 or 0.0364 gram K.

	Calculated for $\text{C}_6\text{H}_3\left(\begin{smallmatrix} \diagup \text{CH}_3 \\ \text{—SO}_3\text{K}+2\text{H}_2\text{O} \\ \diagdown \text{OCH}_3 \end{smallmatrix}\right)$	Found.	
		I.	II.
H_2O	13.05	13.33	13.13
K	14.13	14.00	14.09

Calculated for anhydrous salt, $\text{K} = 16.03$; found, 16.09 and 16.07.

Calcium Salt, $\left(\text{C}_6\text{H}_3\left(\begin{smallmatrix} \diagup \text{CH}_3 \\ \text{—SO}_3 \\ \diagdown \text{OCH}_3 \end{smallmatrix}\right)\right)_2\text{Ca} + 4\frac{1}{2}\text{C}_2\text{H}_5\text{OH}$.—A por-

tion of the free sulphonic acid was dissolved in water, heated, and calcium carbonate added until the solution, on addition of the carbonate, no longer gave off carbon dioxide. On allowing the filtrate to stand, after it was evaporated to concentration, colorless apparently monoclinic prisms separated. On examining these crystals under a petrographical microscope, it was noticed that the extinction angle of several crystals was different from others, and in consequence of this observation, it was believed that a small quantity of gypsum had crystallized with the salt of the sulphonic acid. In order to remove this impurity the crystals were dried in an oven at 180° . They were then dissolved in absolute alcohol, the solution filtered and allowed to evaporate in a vacuum-desiccator. Colorless, transparent crystals separated, which had the appearance of very much distorted octahedrons. After some time it was noticed that acicular crystals began to separate in the same solution. At this point the crystals first formed were removed for analysis. On exposure to the air for a very short time, they became opaque, owing probably, to the rapid loss of their alcohol of crystallization.

Great difficulty was experienced in the analysis of this salt, owing to the fact that the last molecule of alcohol seems to be held more firmly than the others, and comes off only on long continued heating at a high temperature. The heating in several cases was stopped before all the alcohol was driven off, as a slight change in color seemed to indicate that the salt was about to undergo decomposition. The results for calcium in all these cases were low when calculated on the basis of the anhydrous salt; but when the calculation was made on the basis of the hydrous salt, the results for calcium in three cases were constant.

0.2299 gram of salt lost, at 210° , 0.0716 gram alcohol, and gave 0.0485 gram CaSO_4 or 0.01426 gram Ca.

0.161 gram of salt lost, at 210° , 0.0515 gram alcohol, and gave 0.0332 gram CaSO_4 or 0.00976 gram Ca.

Calculated for			
	$\left(\text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{CH}_3 \\ - \text{SO}_2 \\ \diagdown \text{OCH}_3 \end{array} \right)_2 \text{Ca} + 4\frac{1}{2} \text{C}_2\text{H}_5\text{.OH.}$	I.	Found.
			II.
$\text{C}_2\text{H}_5\text{.OH}$	31.41	31.15	31.99
Ca	6.07	6.20	6.06

Calculated on basis of anhydrous salt, $\text{Ca} = 9.03$; found, 9.00 and 8.91.

The needles which separated last were again dissolved after which crystals came down like the crystals first obtained and analyzed. There is reason for the belief that the two forms of crystals obtained were due to the differing concentration of the solution and that the needle-like crystals contained a different number of molecules of alcohol than did those shaped somewhat like the distorted octahedron. (The latter crystals are not octahedrons, but simply present a striking resemblance to distorted octahedrons.) A salt of this nature, concerning which experimental data will be given, will be described later.

The salt which was crystallized from alcohol was powdered and heated for five hours in a drying-oven at 200° , in order to remove the alcohol. It was then dissolved in water and, on slow evaporation, transparent, colorless, long, monoclinic prisms separated. These crystals can remain in the air several days without any sign of efflorescing.

The utmost difficulty was experienced in obtaining anything like satisfactory results for the water contained in the salt. At a temperature of 210° , the salt had a constant weight, but the calcium in every case was about 0.5 per cent. low when calculated on the basis of the anhydrous salt. Long heating at 230° – 240° was found necessary, in order to obtain the salt in an anhydrous condition. Extreme care had to be exercised, as the salt undergoes decomposition at almost the same temperature at which it loses its last trace of water.

0.2364 gram of salt gave 0.0479 gram CaSO_4 or 0.01408 gram Ca.

0.2381 gram of salt lost, at 235° , 0.0795 gram H_2O , and gave 0.0482 gram CaSO_4 or 0.01417 gram Ca.

0.1904 gram of salt lost, at 240° , 0.0622 gram H_2O , and gave 0.0396 gram CaSO_4 or 0.01164 gram Ca.

Calculated for			Found.	
$\left(\text{C}_6\text{H}_5\begin{array}{c} \diagup \text{CH}_3 \\ \text{—SO}_3 \\ \diagdown \text{OCH}_3 \end{array}\right)_2 \text{Ca} + 12\text{H}_2\text{O}.$			II.	III.
	I.			
H_2O	32.83		33.39	32.66
Ca	6.08	5.96	5.95	6.11

Magnesium Salt, $\left(\text{C}_6\text{H}_5\begin{array}{c} \diagup \text{CH}_3 \\ \text{—SO}_3 \\ \diagdown \text{OCH}_3 \end{array}\right)_2 \text{Mg} + 8\text{H}_2\text{O}$. — To a hot

aqueous solution of the free sulphonic acid, finely powdered magnesium oxide was added until the solution was exactly neutral. Light red, transparent, elongated prisms separated which on second crystallization were obtained in a colorless condition. The salt on long exposure to air lost part of its water of crystallization. The anhydrous salt on exposure to air again took up water, but the amount it absorbed was not determined.

0.2142 gram of salt lost, at 150° , 0.0546 gram H_2O , and gave 0.0146 gram MgO or 0.00876 gram Mg.

0.202 gram of salt lost, at 150° , 0.051 gram H_2O , and gave 0.0137 gram MgO or 0.0082 gram Mg.

Calculated for			Found.	
$\left(\text{C}_6\text{H}_5\begin{array}{c} \diagup \text{CH}_3 \\ \text{—SO}_3 \\ \diagdown \text{OCH}_3 \end{array}\right)_2 \text{Mg} + 8\text{H}_2\text{O}$			I.	II.
H_2O	25.26	25.24		25.49
Mg	4.21	4.09		4.07

Calculated for anhydrous salt, $\text{Mg} = 5.63$; found, 5.45 and 5.49.

Copper Salt, $\left(\text{C}_6\text{H}_5\begin{array}{c} \diagup \text{CH}_3 \\ \text{—SO}_3 \\ \diagdown \text{OCH}_3 \end{array}\right)_2 \text{Cu} + 6\frac{1}{2}\text{H}_2\text{O}$. — Two copper

salts were made. The one by exactly precipitating the barium, in an aqueous solution of the barium salt, by means of a dilute solution of copper sulphate, and allowing the copper salt to crystallize slowly after filtering off the barium sul-

phate. The salt thus obtained had a slight blue color and was composed of needles.

Another salt was made by neutralizing the aqueous solution of the free sulphonic acid with freshly prepared copper oxide. The crystals of the salt thus prepared were needles having a slight green color. Probably neither of the salts were pure, but analyses showed both to be identical in composition. The results given under I and II are for the salt prepared by the second method; that under III for the salt made by neutralizing the barium salt with copper sulphate.

0.2286 gram of salt lost, at 150° , 0.0461 gram H_2O , and gave 0.0312 gram CuO or 0.0249 gram Cu .

0.1803 gram of salt lost, at 150° , 0.0361 gram H_2O , and gave 0.025 gram CuO or 0.0199 gram Cu .

0.1582 gram of salt lost, at 150° , 0.0321 gram H_2O , and gave 0.021 CuO or 0.01675 gram Cu .

	Calculated for		Found.	
	$\left(C_6H_5-\begin{array}{c} \diagup CH_3 \\ SO_3 \\ \diagdown OCH_3 \end{array}\right)_2 Cu + 6\frac{1}{2}H_2O$		II.	III.
H_2O	20.09	20.16	20.02	20.21
Cu	10.85	10.88	11.16	10.59

Calculated for anhydrous salt $Cu = 13.52$; found, 13.69, 13.83 and 13.28.

Zinc Salt, $\left(C_6H_5-\begin{array}{c} \diagup CH_3 \\ SO_3 \\ \diagdown OCH_3 \end{array}\right)_2 Zn + 6\frac{1}{2} H_2O$. — This salt was

prepared by neutralizing an aqueous solution of the free acid with zinc carbonate. After recrystallizing the yellow crystals which first separated, perfectly colorless prisms were obtained. The crystals effloresce on exposure to air.

0.208 gram of salt lost, at 125° , 0.0421 gram H_2O , and gave 0.0282 gram ZnO or 0.02363 gram Zn .

0.2041 gram of salt lost, at 125° , 0.0411 gram H_2O , and gave 0.0278 gram ZnO or 0.0223 gram Zn .

Calculated for			
	$\left(\text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{CH}_3 \\ \text{—SO}_3 \\ \diagdown \text{OCH}_3 \end{array} \right)_2 \text{Zn} + 6\frac{1}{2}\text{H}_2\text{O}.$	I.	Found.
			II.
H ₂ O	20.03	20.24	20.13
Zn	11.13	11.36	10.93

Lead Salt, $\left(\text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{CH}_3 \\ \text{—SO}_3 \\ \diagdown \text{OCH}_3 \end{array} \right)_2 \text{Pb} + 3\text{H}_2\text{O}.$ —The lead salt was

prepared by adding lead carbonate to a hot aqueous solution of the free acid. The crystals separating at first were composed of light yellow, radiating fibers. These crystals were dissolved in strong alcohol in order to remove any lead carbonate or sulphate which might have crystallized with them. The alcoholic solution was then evaporated to dryness, and the salt again crystallized from water from which it was obtained in colorless needles which radiated from a central point.

0.2102 gram of salt lost, at 115°, 0.0169 gram H₂O, and gave 0.0964 gram PbSO₄ or 0.06579 gram Pb.

0.230 gram of salt lost, at 115°, 0.0185 gram H₂O, and gave 0.1057 gram PbSO₄ or 0.07214 gram Pb.

Calculated for			
	$\left(\text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{CH}_3 \\ \text{—SO}_3 \\ \diagdown \text{OCH}_3 \end{array} \right)_2 \text{Pb} + 3\text{H}_2\text{O}.$	I.	Found.
			II.
H ₂ O	8.15	8.04	8.05
Pb	31.16	31.30	31.37

Calculated for anhydrous salt, Pb = 34.02; found, 34.11 and 34.02.

Fusion of Paramethoxymetatoluenesulphonic Acid with Potassium Hydroxide.

About 30 grams of potassium hydroxide were melted in a silver crucible and about 10 grams of the free acid, dissolved in water, were gradually added, after the temperature had fallen sufficiently to prevent spurting. The melt assumed a dark red color, and after being heated for one half hour at 180°–200°, gradually turned white, which indicated that some change had taken place. A small portion of the melt

was taken out, dissolved in water and acidified with dilute hydrochloric acid. No odor of sulphur dioxide being perceptible, the fusion was continued, tests for sulphur dioxide being made at intervals of about five minutes. After heating for about an hour at the temperature above mentioned, a trace of sulphur dioxide was noticed, when a portion of the melt was dissolved in water and acidified with hydrochloric acid. The fusion was then discontinued, and the entire melt dissolved in water and acidified with hydrochloric acid. Only a small amount of sulphur dioxide was given off. The solution was evaporated to dryness, the residue heated in a drying-oven at 130° , finely powdered, and extracted for ten minutes with boiling absolute alcohol. From the alcoholic filtrate white needles separated. These needles were purified by being again dissolved in absolute alcohol, in which they are difficultly soluble. From concentrated aqueous solutions the substance separates in colorless, orthorhombic prisms. In this manner, crystals $20 \times 5 \times 2$ millimeters, were obtained. Analysis showed the substance to be a potassium salt. The salt crystallized from water melts at 244° , and decomposes at 247° . The twin crystals form crosses and, in appearance, resemble the mineral staurolite.

0.2164 gram salt gave off, at 170° , 0.0297 gram H_2O , and gave 0.0715 gram K_2SO_4 or 0.03204 gram K.

0.226 gram salt lost, at 190° , 0.0319 gram H_2O , and gave 0.075 gram K_2SO_4 or 0.03361 gram K. The salt in this determination was slightly fused, which accounts for the high result for H_2O .

Calculated for			
$C_6H_5-\begin{array}{c} \diagup CH_3 \\ SO_2OK+2H_2O. \\ \diagdown OH \end{array}$			
		I.	Found.
			II.
H_2O	13.74	13.77	14.11
K	14.88	14.83	14.81

Calculated for anhydrous salt, $K = 17.26$; found, 17.16 and 17.31.

Further Action of Potassium Hydroxide on Paramethoxymetatoluenesulphonic Acid.

From the experiment above described it will be seen that the methoxy group is the least stable, and is most easily replaced by hydroxyl. The sulphonic acid group is very stable in this compound, and it requires a high temperature and fusion for about two hours to replace it by hydroxyl. The fused mass, after reaching the state in the experiment above described, must be stirred constantly to prevent charring. It finally turns deep brown, and becomes liquid, the change from the white pasty mass to the semi-liquid condition being indicative of the complete replacement of the SO_2OH group by OH . As soon as the fusion assumed a liquid condition the heating was discontinued and the melt allowed to cool. It was then dissolved in water and acidified with hydrochloric acid and the solution extracted with ether. On evaporating the ether extract a small quantity of a heavy, dark-colored oil was obtained. It was evidently impure, but the quantity was not sufficient to purify. The aqueous solution of this oil reduced an ammoniacal solution of silver nitrate and also Fehling's solution, and it gave a green color with ferric chloride. This agrees for the color reactions given for homopyrocatechol (methyl-1-dioxy-3-4-benzene), but is not regarded as conclusive evidence that the substance is homopyrocatechol. Homopyrocatechol¹ is described as a brown syrup which, if distilled under diminished pressure, can be purified and made to solidify to a white mass which melts at $49^\circ\text{--}50^\circ$, and boils at $250^\circ\text{--}252^\circ$. It can be obtained in this condition only with great difficulty, and is generally obtained as a brown oil and recognized by its color reactions.

Preparation of Paramethoxymetatoluenesulphone Chloride.

The sodium salt of paramethoxymetatoluenesulphonic acid was dried at 120° , finely powdered, and placed in a porcelain dish. To this salt an equal weight of phosphorus pentachlo-

¹ Compt. rend., **115**, 234; **116**, 104; **118**, 809; **114**, 1543; Ber. d. chem. Ges., **10**, 210; J. Chem. Soc., **55**, 90; Ber. d. chem. Ges., **25**, 3533.

ride was added and the mixture rubbed with a pestle. In a short time action took place and the mass turned into a light yellow, oily material which, on cooling, became solid. It was then washed with water and a portion dissolved in benzene, from which it crystallizes in light yellow plates. It is soluble in ether and acetone. From the latter solvent perfectly colorless, transparent plates can be obtained if the solution is evaporated slowly in a vacuum-desiccator. These plates melt at 83.5° – 84° . The same specimen after it was allowed to cool again melted at the same point.

0.1852 gram of the chloride gave 0.1199 gram silver chloride, or 0.02966 gram chlorine.

	Calculated for	
	$\begin{array}{c} \diagup \text{CH}_3 \\ \text{C}_6\text{H}_5-\text{SO}_2\text{Cl} \\ \diagdown \text{OCH}_3 \end{array}$	
Cl	16.06	Found. 16.02

Preparation of Paramethoxymetatoluenesulphone Amide.

The chloride obtained as above described was finely powdered and 50 grams of it were placed in a beaker containing about 300 cc. strong ammonia and 200 cc. water. No immediate action was observed to take place, but on allowing to stand over night it was noticed that the mass at the bottom of the beaker had changed from white to a dark yellow color. This yellow mass was removed and crystallized from boiling water, from which it separates in needles which melt at 180° – 181° . It is insoluble in cold water, and soluble with great difficulty in boiling water. It is easily soluble in hot alcohol, which is the best solvent for its purification. From alcohol it separates in white needles. The ammoniacal solution was evaporated to dryness, and on the addition of cold water nearly the entire residue went into solution, showing that the amide is practically insoluble in ammonia.

0.2073 gram of amide gave 0.2415 gram BaSO_4 .

0.219 gram of amide gave 0.2516 gram BaSO_4 .

0.2835 gram of amide gave 0.0205464 gram nitrogen.

Calculated for $\text{C}_6\text{H}_5-\begin{array}{c} \diagup \text{CH}_3 \\ \text{SO}_2\text{NH}_2 \\ \diagdown \text{OCH}_3 \end{array}$				
		I.	Found. II.	III.
S	15.92	15.98	15.77	
N	6.96			7.21

Preparation of Paramethoxymetasulphaminebenzoic Acid.

In a long-necked balloon flask, of 3 liters capacity, 180 grams of potassium permanganate were placed and 2 liters of water added. To this solution 50 grams of paramethoxymetatoluenesulphonamide were added, the flask provided with a return-condenser, placed in a water-bath, and heated till the potassium permanganate was completely reduced. By this treatment it was expected that the methyl group would be oxidized to carboxyl.

When the blue color had entirely disappeared the manganese hydroxide was filtered off and thoroughly washed with hot water. Strong hydrochloric acid was then added to the filtrate, and white needles separated. In order to remove any unoxidized amide, the material thus obtained was dissolved in dilute sodium carbonate in which the amide is insoluble. On addition of hydrochloric acid to the solution the free acid again separated and was then crystallized from boiling water, in which it is sparingly soluble. Thus obtained, it melted at 252°-277°, and repeated recrystallizations from water did not give a pure product. It was then dissolved in boiling absolute alcohol and obtained from this in a pure condition. Thus purified, it melted at 276°-277°. At 274° there was a slight change in color, but no evidence of melting was observed on keeping the temperature at that point for some time. From alcohol both needles and plates were obtained from the same solution, but the melting-point of each indicated that they were identical except in crystal form. As a result of several experiments, it is believed that when the temperature of the water-bath, in which the flask is placed during the oxidation process, is not raised above 85°, the yield of the oxidation product is greater than if the water in the bath be allowed to boil constantly. Almost a quantitative yield was obtained

by slow oxidation at 85°, whereas, when the temperature was raised to about 100° the product yielded was less than half of the theoretical.

0.2968 gram of acid gave 0.0186 gram of nitrogen.

0.3055 gram of acid gave 0.019177 gram of nitrogen.

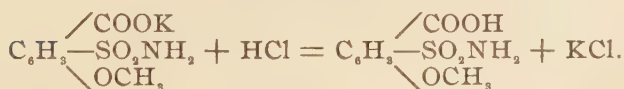
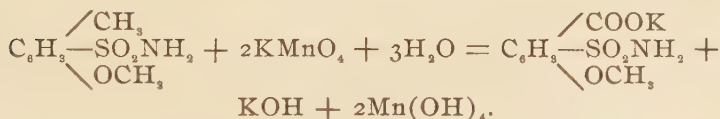
0.2521 gram of acid gave 0.2554 gram BaSO₄.

0.2802 gram of acid gave 0.2838 gram BaSO₄.

0.2026 gram of acid gave 0.3062 gram of CO₂, and 0.0733 gram H₂O.

Calculated for C ₆ H ₃ $\begin{array}{l} \diagup \text{COOH} \\ \text{—SO}_2\text{NH}_2 \\ \diagdown \text{OCH}_3 \end{array}$		I.	II.	Found. III.	IV.	V.
C	41.56	41.21				
H	3.89	4.02				
N	6.06		6.27	6.28		
S	13.85				13.91	13.97

The following equations probably represent what took place :



Salts of Paramethoxymetasulphaminebenzoic Acid.

Sodium Salt, C₆H₃ $\begin{array}{l} \diagup \text{COONa} \\ \text{—SO}_2\text{NH}_2 \\ \diagdown \text{OCH}_3 \end{array}$ + 3H₂O.—This salt was made

by neutralizing a boiling solution of the free acid with sodium carbonate. It separates in needles which have a slight cream color, but are transparent. The salt is insoluble in strong hot alcohol.

0.2364 gram of salt lost, at 160°, 0.0372 gram H₂O, and gave 0.0557 gram Na₂SO₄ or 0.01803 gram Na.

0.2623 gram of salt lost, at 160°, 0.0414 gram H₂O, and gave 0.062 gram Na₂SO₄ or 0.02068 gram Na.

	Calculated for $\text{C}_6\text{H}_5\text{—}\begin{array}{c} \diagup \text{COONa} \\ \text{SO}_2\text{NH}_2 \\ \diagdown \text{OCH}_3 \end{array} + 3\text{H}_2\text{O}.$	I.	Found.	II.
H ₂ O	15.95	15.74		15.79
Na	7.64	7.62		7.65

Calculated for anhydrous salt Na = 9.09; found 9.06 and 9.08.

Potassium Salt, $\text{C}_6\text{H}_5\text{—}\begin{array}{c} \diagup \text{COOK} \\ \text{SO}_2\text{NH}_2 \\ \diagdown \text{OCH}_3 \end{array} + 1\frac{1}{2}\text{H}_2\text{O}$.—The potassium

salt was made by neutralizing the hot aqueous solution of the free acid with potassium carbonate. It crystallizes from water in extremely fine, almost colorless, needles. It is very soluble in water and good crystals are difficult to obtain. The salt thus made was found to contain potassium carbonate, and in order to purify it it was dissolved in hot 90 per cent. alcohol, from which small white needles were obtained, which melted at 262°, with decomposition. It is insoluble in cold alcohol.

0.3046 gram of salt lost, at 210°, 0.0276 gram H₂O, and gave 0.0889 gram K₂SO₄ or 0.03985 gram K.

0.2886 gram of salt lost, at 210°, 0.0263 gram H₂O, and gave 0.0842 gram K₂SO₄ or 0.0377 gram K.

	Calculated for $\text{C}_6\text{H}_5\text{—}\begin{array}{c} \diagup \text{COOK} \\ \text{SO}_2\text{NH}_2 \\ \diagdown \text{OCH}_3 \end{array} + 1\frac{1}{2}\text{H}_2\text{O}.$	I.	Found.	II.
H ₂ O	9.12	9.06		9.11
K	13.18	13.08		13.08

Calculated for anhydrous salt K = 14.49; found, 14.39 and 14.39.

Calcium Salt, $\left(\text{C}_6\text{H}_5\text{—}\begin{array}{c} \diagup \text{COO} \\ \text{SO}_2\text{NH}_2 \\ \diagdown \text{OCH} \end{array}\right)_2\text{Ca} + 5\text{H}_2\text{O}$.—This salt

was prepared by adding finely powdered calcite to a boiling solution of the free acid until the solution was just neutral.

The first crystals were rejected as probably impure. The last crystals separated as white, glistening needles, arranged in clusters. The salt can be exposed to air without losing its water. It is insoluble in cold or hot strong alcohol.

0.2195 gram of salt lost, at 235° , 0.0335 gram H_2O , and gave 0.0497 gram $CaSO_4$ or 0.01461 gram Ca.

0.2245 gram of salt lost, at 235° , 0.0341 gram H_2O , and gave 0.0503 gram $CaSO_4$ or 0.01479 gram Ca.

Calculated for		Found.	
$(C_6H_5-\begin{smallmatrix} \diagup COO \\ SO_2NH_2 \\ \diagdown OCH_3 \end{smallmatrix})_2 Ca + 5H_2O.$		I.	II.
H_2O	15.25	15.27	15.19
Ca	6.77	6.65	6.59

Calculated for anhydrous salt, Ca = 8.00; found, 7.96 and 7.77.

Barium Salt, $(C_6H_5-\begin{smallmatrix} \diagup COO \\ SO_2NH_2 \\ \diagdown OCH_3 \end{smallmatrix})_2 Ba + 4\frac{1}{2}H_2O.$ —A boiling

solution of the free acid in water was neutralized with finely powdered barium carbonate. On filtering and evaporating, fine, white needles were obtained. The crystals radiated from the center, and in form resembled a chestnut burr. The salt is almost insoluble in alcohol but easily soluble in cold water—not nearly so soluble, however, as the corresponding salt of the free sulphonic acid. In order to completely dehydrate the salt it was necessary to heat it for a long time at 245° . It decomposes at about 255° .

0.3400 gram of salt lost, at 245° , 0.041 gram H_2O , and gave 0.1174 gram $BaSO_4$ or 0.069 gram Ba.

0.3314 gram salt lost, at 245° , 0.0396 gram H_2O , and gave 0.1154 gram $BaSO_4$ or 0.0679 gram Ba.

Calculated for		Found.	
$(C_6H_5-\begin{smallmatrix} \diagup COO \\ SO_2NH_2 \\ \diagdown OCH_3 \end{smallmatrix})_2 Ba + 4\frac{1}{2}H_2O.$		I.	II.
H_2O	11.93	12.06	11.95
Ba	20.29	20.33	20.49

Calculated for anhydrous salt, Ba = 23.00; found, 23.11 and 23.24.

Magnesium Salt, $\left(\text{C}_6\text{H}_3 \begin{array}{l} \diagup \text{COO} \\ - \text{SO}_2\text{NH}_2 \\ \diagdown \text{OCH}_3 \end{array} \right)_2 \text{Mg} + 6\text{H}_2\text{O}$. — To a

boiling solution of the free acid, finely powdered magnesium carbonate was added until the solution was neutral. Fine, silky needles separated at first. These needles, on removal for the purpose of drying, were accidentally placed in a warm place and they went into solution. From this concentrated solution colorless crystals, which have the appearance of thick triclinic prisms, separated. These crystals were remarkable for their iridescence. It was noticed that from the same solution both needles and prisms would separate, only a few prisms crystallizing when the solution was dilute and the needles compact. Analysis of the prism crystals gave the following result :

0.2901 gram of salt lost, at 225°, 0.0521 gram H₂O, and gave 0.0201 gram MgO or 0.01207 gram Mg.

0.2328 gram of salt lost, at 235°, 0.0428 gram H₂O.

0.2533 gram of salt gave 0.0172 gram MgO or 0.01033 gram Mg.

It was found necessary to add fine ammonium carbonate in order to get rid of the sulphonic acid residue. Without this addition the results for magnesium were high, showing that magnesium sulphate had probably been formed.

Calculated for		Found.	
$\left(\text{C}_6\text{H}_3 \begin{array}{l} \diagup \text{COO} \\ - \text{SO}_2\text{NH}_2 \\ \diagdown \text{OCH}_3 \end{array} \right)_2 \text{Mg} + 6\text{H}_2\text{O}$		I.	II.
H ₂ O	18.24	17.96	18.34
Mg	4.05	4.16	4.08

Analysis of the air-dried acicular crystals indicated that they contained 10½ molecules of water. Both kinds of crystals were exposed to the air without losing their water of crystallization.

Fusion of Paramethoxymetasulphaminebenzoic Acid with Potassium Hydroxide.

About 40 grams of potassium hydroxide were heated with a little water in a silver dish until the alkali was dissolved. About 5 grams of the paramethoxymetasulphaminebenzoic acid were then added. The addition of the acid is most conveniently made by first dissolving it in aqueous potassium hydroxide and then adding the solution slowly. The fusion was carried on for about twenty minutes, care being taken to avoid too high temperature in order that the compound might not be entirely broken down. The melt was then dissolved in water and acidified with hydrochloric acid. No odor of sulphur dioxide was perceptible, showing that the group SO_2NH_2 had not been replaced by hydroxyl. On standing for some time in a cool place, white needles separated. The crystals were arranged in radiating clusters and had a more blunt, prism-like appearance than has the corresponding methoxy compound. The compound crystallizes well from alcohol, and is more soluble in water than the paramethoxymetasulphaminebenzoic acid. Its melting-point is 258° , and it decomposes at about 265° . Analysis shows it to be parahydroxymetasulphaminebenzoic acid.

0.3049 gram of acid gave 0.01999 gram of nitrogen.

0.3065 gram of acid gave 0.02033 gram of nitrogen.

0.2022 gram of acid gave 0.0528 gram H_2O or 0.00587 gram H, and 0.285 gram CO_2 or 0.0777 gram C.

0.2413 gram of acid gave 0.2605 gram BaSO_4 or 0.0358 gram S.

Calculated for		Found.			
$\text{C}_6\text{H}_5\begin{matrix} \diagup \text{COOH} \\ \text{—SO}_2\text{NH}_2 \\ \diagdown \text{OH} \end{matrix}$		I.	II.	III.	IV.
C	38.76				38.44
H	3.22				2.90
N	6.45	6.56	6.63		
S	14.75			14.83	

Salts of Parahydroxymetasulphaminebenzoic Acid.

Sodium Salt, $\text{C}_6\text{H}_5\text{—}\begin{array}{c} \diagup \text{COONa} \\ \text{—SO}_2\text{NH}_2 \\ \diagdown \text{OH} \end{array} + 4\text{H}_2\text{O}$.—This salt was made

by neutralizing a hot solution of the acid with sodium carbonate. The white, radiating needles obtained are very soluble in water but insoluble in boiling, strong alcohol.

0.2203 gram of salt lost, at 170° , 0.0506 gram H_2O , and gave 0.0499 gram Na_2SO_4 or 0.01616 gram Na.

	Calculated for $\text{C}_6\text{H}_5\text{—}\begin{array}{c} \diagup \text{COONa} \\ \text{—SO}_2\text{NH}_2 \\ \diagdown \text{OH} \end{array} + 4\text{H}_2\text{O}$	Found.
H_2O	23.15	22.97
Na	7.40	7.34

Barium Salt, $\left(\text{C}_6\text{H}_5\text{—}\begin{array}{c} \diagup \text{COO} \\ \text{—SO}_2\text{NH}_2 \\ \diagdown \text{OH} \end{array}\right)_2\text{Ba} + 6\frac{1}{2}\text{H}_2\text{O}$. — The ba-

rium salt was made by neutralizing the hot aqueous solution of the free acid with finely-powdered barium carbonate. It separated in white tufts which are easily soluble in water and insoluble in boiling alcohol.

0.2381 gram of salt lost, at 240° , 0.0403 gram H_2O , and gave 0.0812 gram BaSO_4 , or 0.0478 gram Ba.

	Calculated for $\left(\text{C}_6\text{H}_5\text{—}\begin{array}{c} \diagup \text{COO} \\ \text{—SO}_2\text{NH}_2 \\ \diagdown \text{OH} \end{array}\right)_2\text{Ba} + 6\frac{1}{2}\text{H}_2\text{O}$	Found.
H_2O	17.03	16.93
Ba	20.01	20.06

It is probable that neither of the two salts of the hydroxy acid were pure. Lack of material prevented the preparation of other salts.

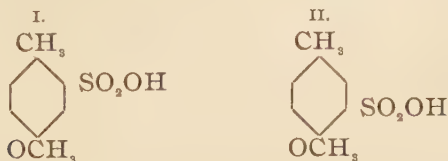
Further Action of Potassium Hydroxide on Paramethoxymetasulphaminebenzoic Acid.

It was found in a previous experiment that the methoxy group in the methoxysulphamine acid could be replaced by

hydroxyl without the removal of the sulphamine group. In order to test the further action of potassium hydroxide on this acid, 20 grams of potassium hydroxide were placed, together with a little water, in a silver dish and melted. To this melt about 3 grams of the methoxysulphamine acid were gradually added, and the mass fused, at a high temperature, for about two hours. On dissolving the melt, and acidifying it with hydrochloric acid, sulphur dioxide was given off in abundance. The acidified solution was then extracted with ether, the ether evaporated, and a dark semi-crystalline mass obtained. This was dissolved in alcohol, from which it separated in yellow crystals which melted at 187° – 192° . This material reduced an ammoniacal solution of silver nitrate, but had no effect on Fehling's solution. Ferric chloride added to an aqueous solution of the substance produced a blue-green color which turned red on the addition of sodium carbonate. This is clear evidence that the substance is protocatechuic acid, and is, therefore, confirmatory evidence that the sulphamine group is in the meta position.

Discussion of the Evidence which Shows that the Sulphonic Acid Group in Paramethoxymetatoluenesulphonic Acid is in the Meta Position.

There are two possibilities for the entrance of a single SO_2OH group, in paramethoxytoluene, which may be represented by formulas I and II.



The first, by the replacement of the methoxy and sulphamine groups by hydroxyl, by fusion with potassium hydroxide, should yield methyl-1-dioxy-2-4-benzene; the second by similar treatment should give homopyrocatechol or methyl-1-dioxy-3-4-benzene. It is believed that the latter product was

obtained, but the evidence is not as conclusive as might be desired.

By treatment with phosphorus pentachloride, the sodium salt of the sulphonic acid I should yield a chloride,

$\text{C}_6\text{H}_5-\begin{array}{c} \diagup \text{CH}_3 \\ \text{SO}_2\text{Cl} \\ \diagdown \text{OCH}_3 \end{array}$ (*o*), and this, on treatment with ammonia, should

give the amide, $\text{C}_6\text{H}_5-\begin{array}{c} \diagup \text{CH}_3 \\ \text{SO}_2\text{NH}_2 \\ \diagdown \text{OCH}_3 \end{array}$ (*o*). On oxidizing this amide

with potassium permanganate a sulphinide would be obtained

having the formula $\text{C}_6\text{H}_5-\begin{array}{c} \diagup \text{CO} \\ \text{SO}_2 \\ \diagdown \text{OCH}_3 \end{array} > \text{NH}$. All these compounds

were made by Parks,¹ working in this laboratory. The compounds which Parks obtained agree in no respect with those obtained by the writer. The chloride made by Parks is an oil; the amide is composed of white needles and melts at 150°, and the sulphinide, of needles which melt at 271°.

Metcalf,² working in this laboratory, by diazotizing para-toluidinemetasulphonic acid, decomposing the product with methyl alcohol, and then treating the sodium salt of the resulting compound with phosphorus pentachloride, obtained a

chloride which had the formula $\text{C}_6\text{H}_5-\begin{array}{c} \diagup \text{CH}_3 \\ \text{SO}_2\text{Cl} \\ \diagdown \text{OCH}_3 \end{array}$ (*m*). From this

chloride he obtained the amide $\text{C}_6\text{H}_5-\begin{array}{c} \diagup \text{CH}_3 \\ \text{SO}_2\text{NH}_2 \\ \diagdown \text{OCH}_3 \end{array}$ (*m*), and on

oxidizing this a compound which he took to be

$\text{C}_6\text{H}_5-\begin{array}{c} \diagup \text{COOH} \\ \text{SO}_2\text{NH}_2 \\ \diagdown \text{OCH}_3 \end{array}$ (*m*), although it was impure, as indicated by

its melting-point.

The compounds the writer obtained agree with those which Metcalf made. In addition to this the writer, by fusing the

acid, $\text{C}_6\text{H}_5-\begin{array}{c} \diagup \text{COOH} \\ \text{SO}_2\text{NH}_2 \\ \diagdown \text{OCH}_3 \end{array}$ (*m*), with potassium hydroxide obtained

¹ Am. Chem. J., 15, 320.

² *Ibid*, 15, 301.

protocatechuic acid, $C_6H_3 \begin{array}{l} \diagup \text{COOH} \\ \text{—OH}(m) \\ \diagdown \text{OH}(p) \end{array}$. All these facts agree

with the assumption that the group SO_3OH entered in the meta position, and that the sulphonic acid first formed is that indicated by formula II, or paramethoxymetatoluenesulphonic acid.

Summary of Results.

1. When paradiazotoluene sulphate is decomposed, at the ordinary pressure, with methyl alcohol in the presence of the compounds formed during the diazotizing process, both the methoxy and hydrogen reactions take place; the latter, however, to a very small extent.

2. When paramethoxytoluene is treated with sulphuric acid, but one sulphuric acid residue enters the compound, and the sulphonic acid group is in the meta position.

3. When paramethoxymetatoluenesulphonic acid is slightly fused with potassium hydroxide there results potassium parahydroxymetatoluenesulphonate; on longer fusion homopyrocatechol is obtained.

4. When oxidized with potassium permanganate, paramethoxymetatoluenesulphoneamide yields paramethoxymetasulphaminebenzoic acid.

5. When paramethoxymetasulphaminebenzoic acid is cautiously fused with potassium hydroxide there is obtained parahydroxymetasulphaminebenzoic acid; on prolonged fusion at a high temperature, protocatechuic acid.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE JUNE, 1897.

BIOGRAPHICAL SKETCH.

Gellert Alleman was born in Littlestown, Pa., July 23, 1871. His early education was received in the public schools at York, Pa. In the fall of 1890 he entered Pennsylvania College, at Gettysburg, and received the degree of Bachelor of Science in 1893. From 1893 to 1897 he pursued the studies of chemistry, mineralogy, and physics at the Johns Hopkins University.

